

# **Center of Excellence for the Synthesis and Processing of Advanced Materials: Review – June 12, 2003**

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## **“Defect Structures and Properties in Rare-Earth-Ba-Cu-O Cuprate Superconductors”**

David O. Welch  
Brookhaven National Laboratory  
Project Coordinator

# A Project of the Center of Excellence for the Synthesis and Processing of Advanced Materials:

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“Defect Structures and Properties in Rare-Earth- Ba-Cu-O  
Cuprate Superconductors”

Participating Institutions:

Ames Laboratory, Argonne National Laboratory,  
Brookhaven National Laboratory, Oak Ridge Laboratory,  
Los Alamos National Laboratory, and Sandia National Laboratory

Project Coordinator:

David O. Welch, BNL

# **CSP Review: “Defect Structures... in Cuprate Superconductors”**

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This project involves groups funded by BES and/or the “Superconductivity for Electric Systems” program, Office of Energy Efficiency and Renewable Energy.

New Feature:

Collaboration with AFOSR Coated Conductor MURI

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- “The key to better engineering lies in the knowledge of imperfections in materials”

quoted from an advertisement of a professorship in the  
Materials Science and Technology Department, Faculty of  
Applied Sciences,

TU Delft, Physics Today, February 2001

- “Like people, materials are interesting because of their faults.”

Sir Charles Frank

# Active Collaborative Projects

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- Basic Properties of RE-123 Compounds
  - Substitution Effects on Superconductivity
  - Systematics of Thermophysical Properties

Ames: McCallum, Kramer      ANL: Veal

BNL: Welch, Su (Caltech)

- Defect Structures and Critical Currents in YBCO Coated Conductors

ANL: Miller, Veal

ORNL: Goyal, Christen, Feenstra, Lee

BNL: Suenaga, Welch

LANL: Holesinger, Foltyn

SNL: Clem, Siegal

# **“Collaborations” (cont.)**

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- **Grain boundaries, in YBCO**

ANL:	Veal, Paulikas, Berghuis, Claus, Gray
BNL:	Suenaga, Welch, Su, Zhu
ORNL:	Christen, Goyal
LANL:	Holesinger

- **Flux Pinning**

BNL:	Suenaga, Welch
ORNL:	Christen, Feenstra
LANL:	Foltyn, Holesinger

# Activities

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- “Caucuses” at Fall MRS (November 2002);  
EERE “Superconductivity for Electric Systems” Program Wire Development Workshop (January 2003);  
EE Superconductivity Peer Review (July 2003).
- Workshop on “Zoology and Ecology” of Defects and Nanoscale Structure in 123-Phase Superconductors, BNL, October 2003
- Review article on state-of-the-art

# Some Research Highlights

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- Coated Conductors
- Grain Boundaries
- Flux Pinning



# Coated Conductors

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- Coated Conductor Architecture: Buffer Layers and Defects

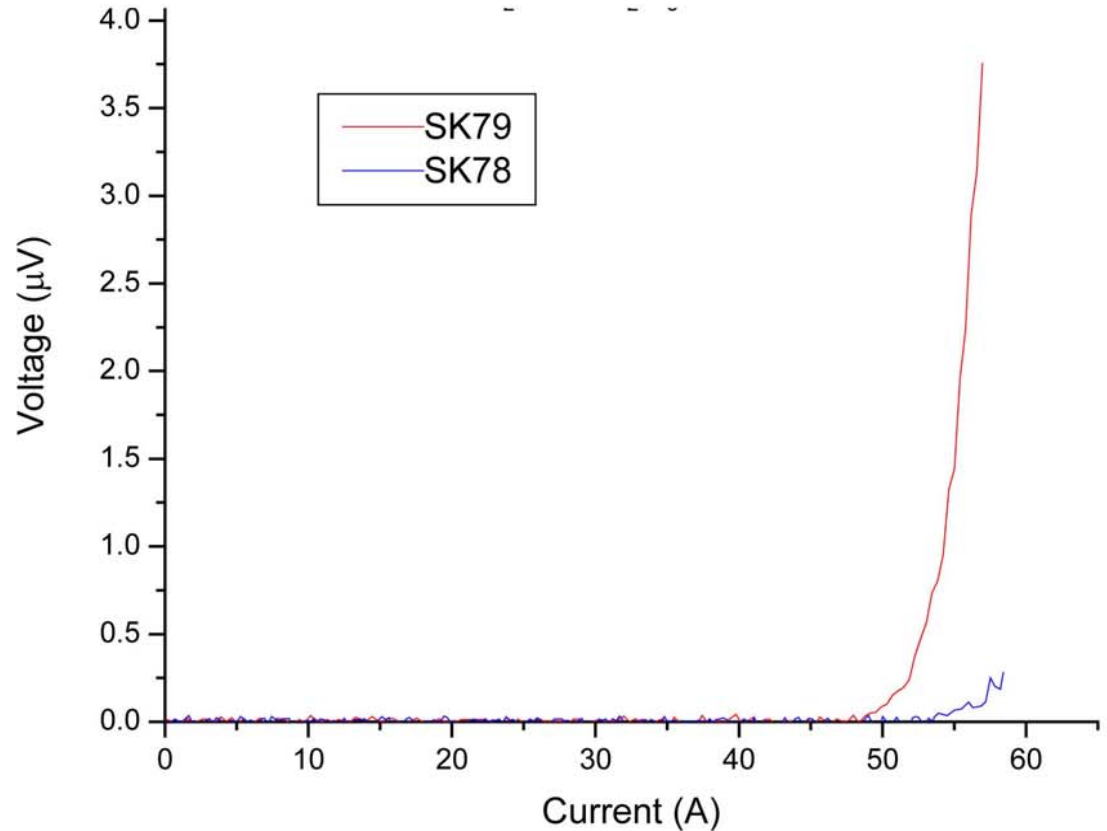
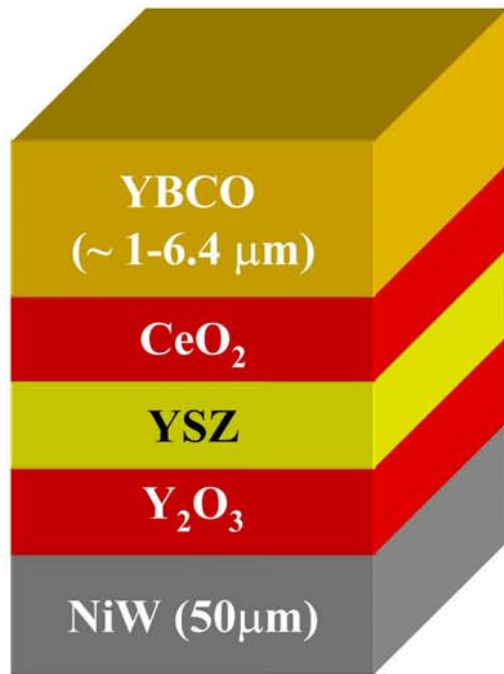
ORNL, LANL, SNL, BNL

- The  $\text{BaF}_2$  process for ex-situ YBCO growth

ANL, BNL, ORNL, SNL, LANL

- Growth and Characterization
- Thickness Dependence of  $J_c$

# PLD YBCO films on buffered Ni-W substrates



Sample No. SK78, 5 mm wide

YBCO Thickness: 1.00  $\mu\text{m}$

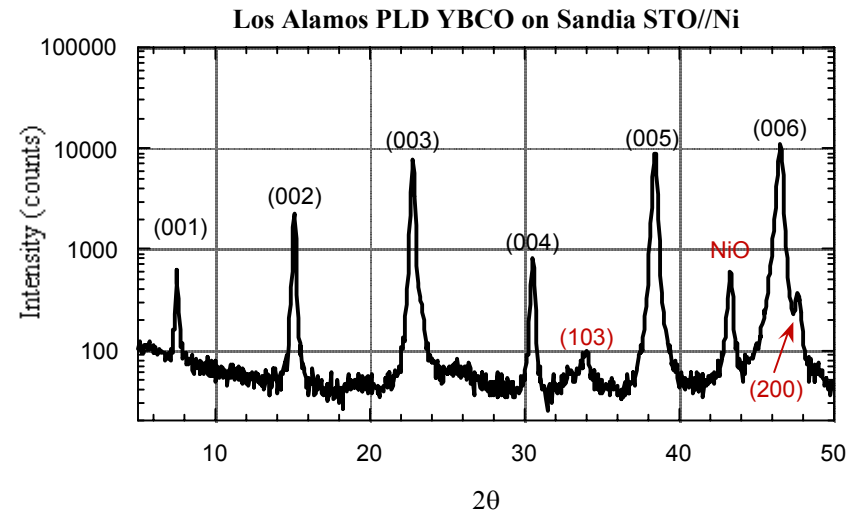
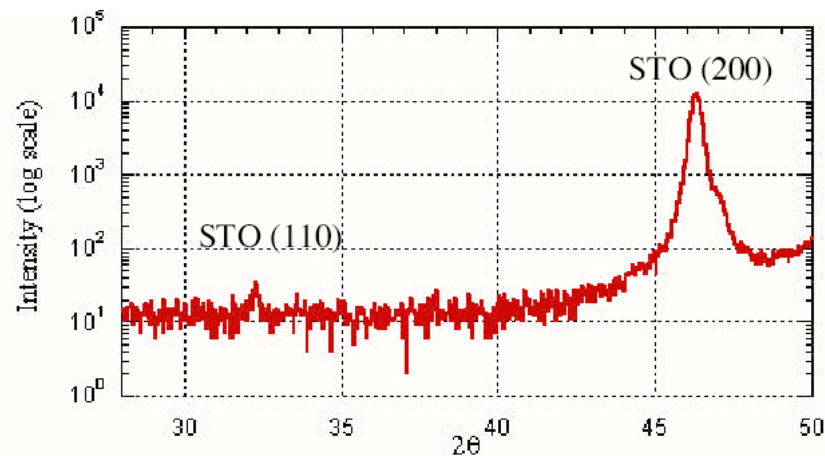
$I_c = 59\text{A}$  (self-field, 77K),  $I_c/\text{width} = 118\text{ A/cm}$ ;  $J_c = 1.18\text{ MA/cm}^2$

# Stress-Induced Nanocracks in YBCO Coated-Conductors Due to Oxygen Diffusion Through STO Buffer Layers

M. Siegal, P. Clem and J. Dawley (Sandia)

S. Folytn and T. Holesinger (Los Alamos)

**Goal: grow thick YBCO films on sol-gel buffered metal tapes**



Highly-oriented STO grows easily on  $\text{Ba}_{0.2}\text{Ca}_{0.8}\text{TiO}_3//\text{Ni}(100)$  templates.

1.3  $\mu\text{m}$  thick YBCO by PLD (LANL)  
on STO/BCT/Ni by sol-gel (SNL)  
*note presence of NiO!*

Great c-axis orientation,  $T_c = 87\text{ K}$ ,  
however  $J_c(75\text{ K}) < 1000\text{ A/cm}^2$ . WHY?

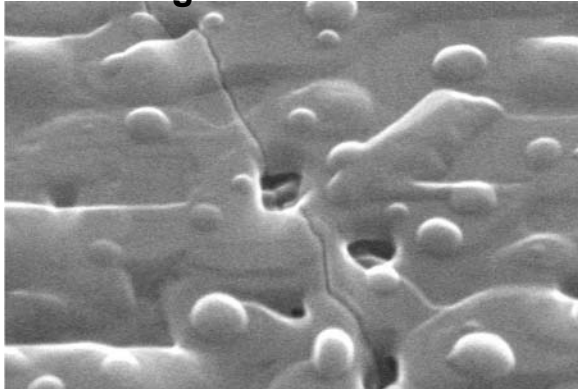


**Nanocracking**

# Nanocracking, Oxygen Diffusion, Stress....

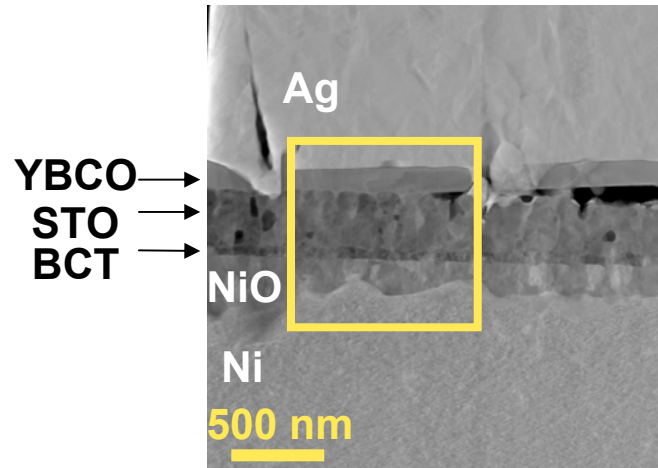
**Nanocracking**  
(from PLD or sol-gel)  
greatly limits supercurrent!

SNL sol-gel YBCO/STO/BCT/Ni



**What causes nanocracking?**

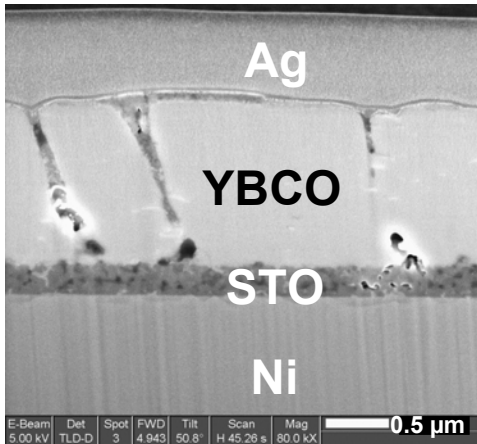
Dark-field STEM image



**Significant NiO at  
buffer/Ni  
interface.**

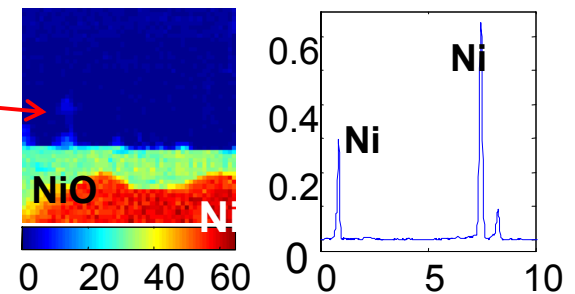
**Resulting YBCO  
layer has  
nanocracks.**

LANL PLD YBCO/STO/BCT/Ni



**note the  
protrusion of  
NiO into the  
STO buffer  
region above  
the substrate**

X-Ray Spectral Image Analysis

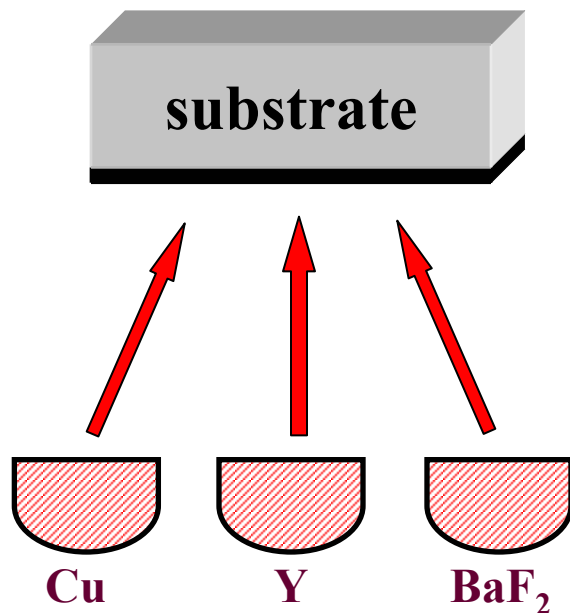


**Different thermal  
expansion coefficients**

***STRESS***

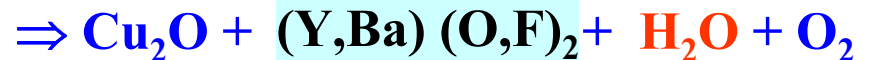
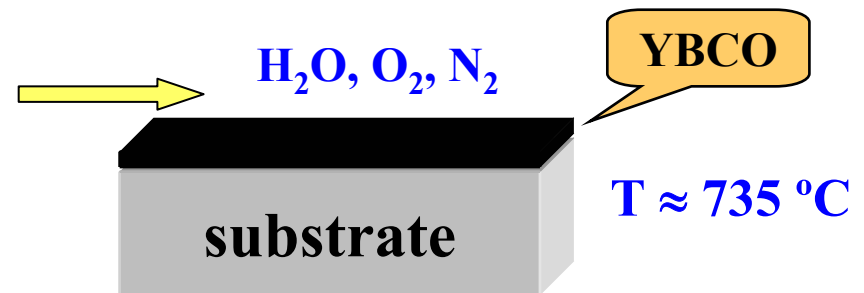
# YBCO Thick Film Synthesis

## YBCO Precursor Deposition E-beam evaporation



*V.F. Solovyov, H.J. Wiesman  
DMCS, BNL*

## Textured YBCO Formation by a post-deposition reaction process

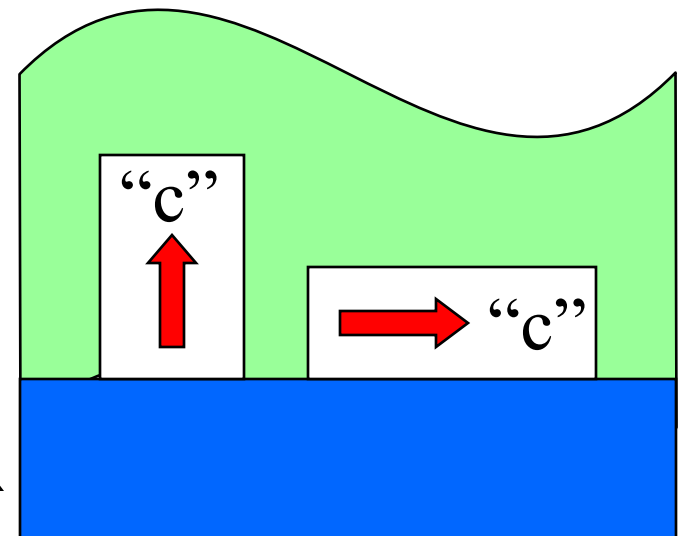
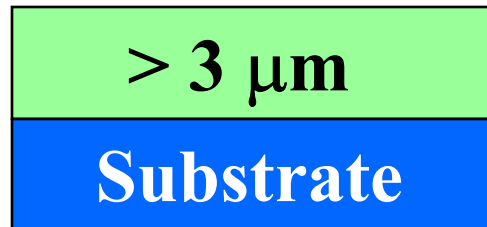


# Nucleation of Epitaxial YBCO

- How does an oxide epitaxially nucleate and grow from a buried interface at the substrate surface ?

A precursor mixture

Cu, Y, & BaF<sub>2</sub>



# Thickness dependence of $J_c$ in YBCO coated conductors

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**Ron Feenstra, A. A. Gapud, D. K. Christen, E. D. Specht, A. Goyal,**  
*Oak Ridge National Laboratory*

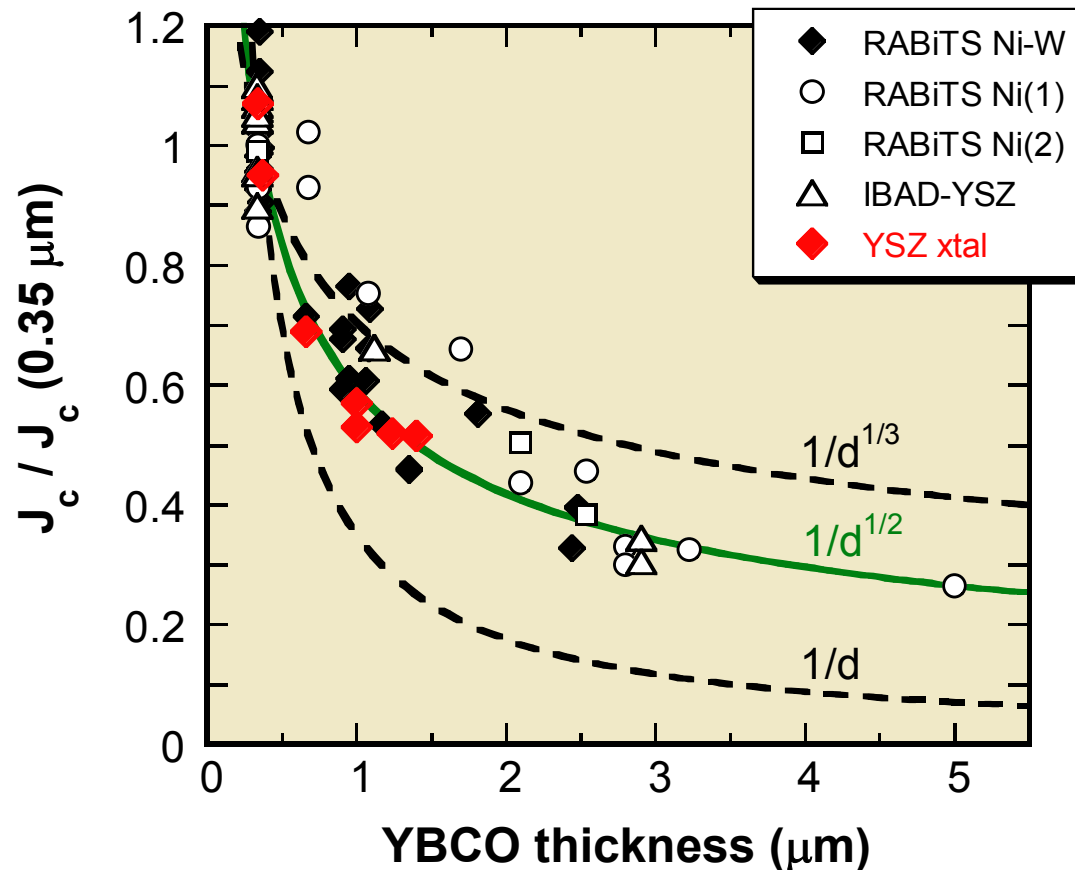
**D. M. Feldmann, D. C. Larbalestier,** *University of Wisconsin*

**T. G. Holesinger, P. N. Arendt,** *Los Alamos National Laboratory*



# Collaborative research is performed to determine intrinsic and materials effects on $J_c(d)$

- YBCO films grown at ORNL (BaF<sub>2</sub> ex situ process)
- through-thickness  $J_c$  (stepwise thinning) measured at UW
- microstructure analyzed at LANL

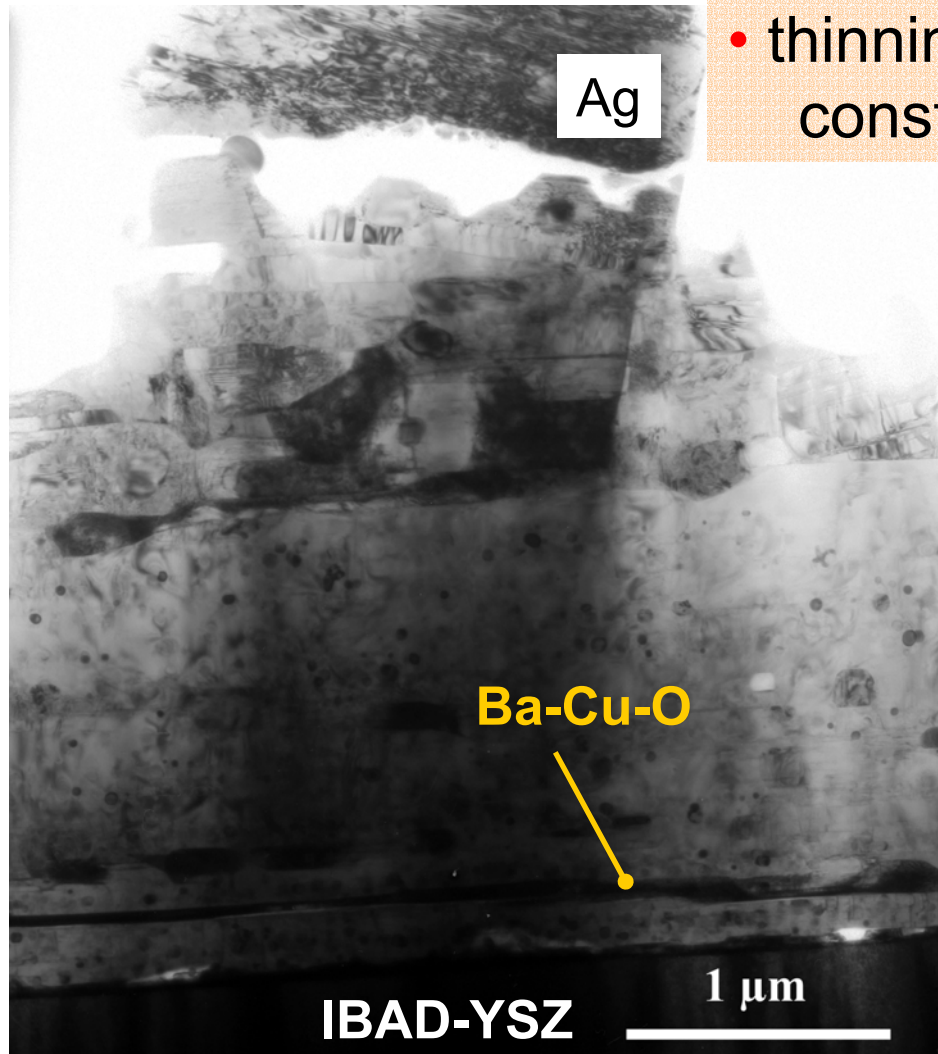


- $J_c(d)$  (on normalized scale) is independent of substrate: RABiTS, IBAD-YSZ, crystal
- $J_c(d) \propto 1/d^{1/2}$ 
  - qualitatively consistent with 2D collective pinning model
- similar  $J_c(d)$  observed for PLD



# TEM reveals bi-layer-like structure in thick YBCO

- suggestive of different growth modes
- thinning study (Univ. Wisconsin) → constant  $J_c$  through thickness



YBCO  
(small-grains)

YBCO (2.9  $\mu\text{m}$ ) / IBAD-YSZ  
 $I_c = 240 \text{ A/cm}$  (77 K)

YBCO  
(large-grains)

$\text{CeO}_2$



# Reel-to-reel characterization of YBCO coated conductors: Formation of YBCO from “BaF<sub>2</sub>” precursor

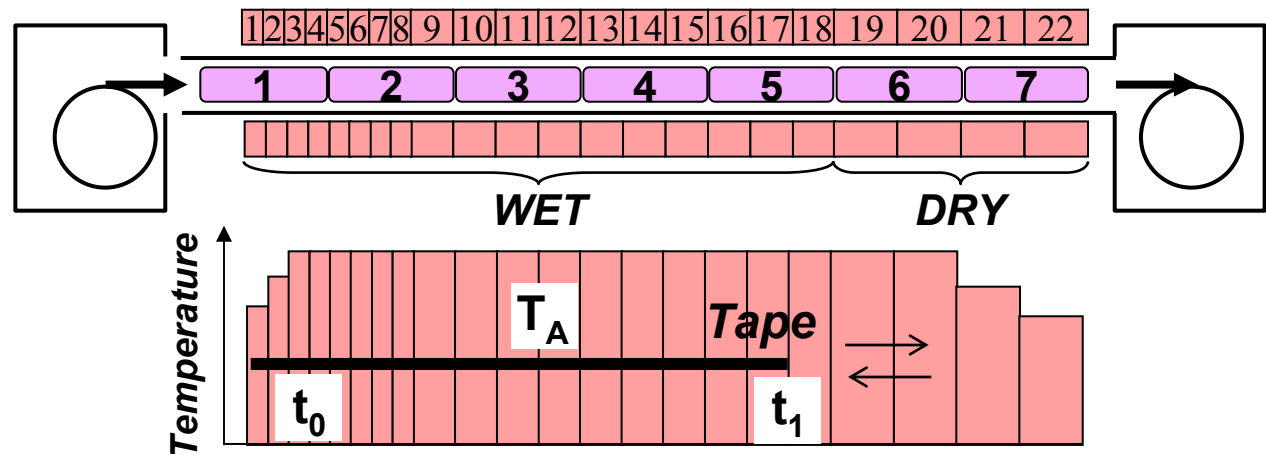
PI's: ANL – V. Maroni ORNL – D. F. Lee

**Objectives:** To study ex-situ YBCO formation using complementary R-R XRD and Raman techniques.

To investigate the possibility of using these techniques for in-situ monitoring.

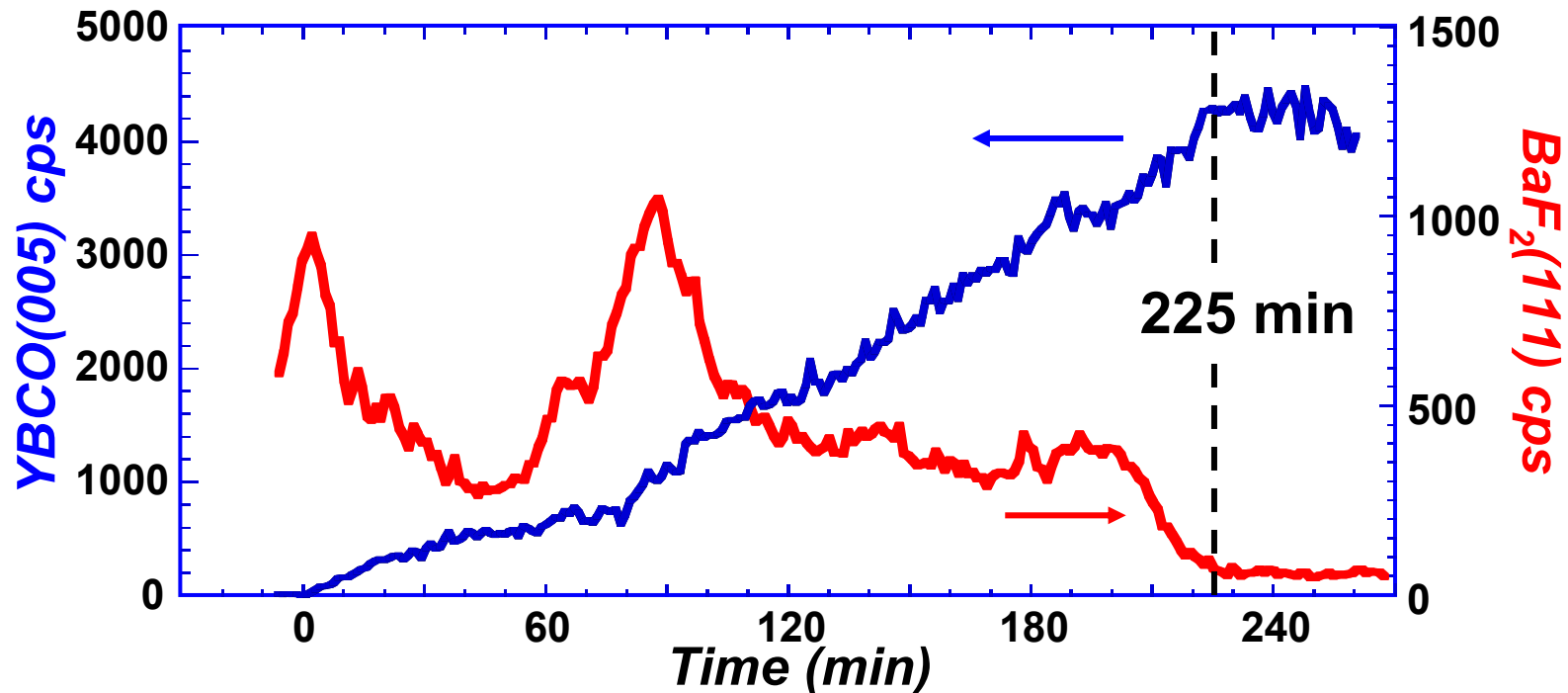
## Sample Preparation

- RABiTS tape with “BaF<sub>2</sub>” precursor is pulled into furnace with a set profile.
- Once the front of the tape has reached time  $t_1$ , the sample is re-wound onto cold payout reel at 2m/min.
- Sample consists of ramp-up section and section in which anneal time at  $T_A$  varies from zero to  $t_1 - t_0$



# Reel-to-Reel XRD has been shown to be invaluable In aiding the optimization of processing conditions

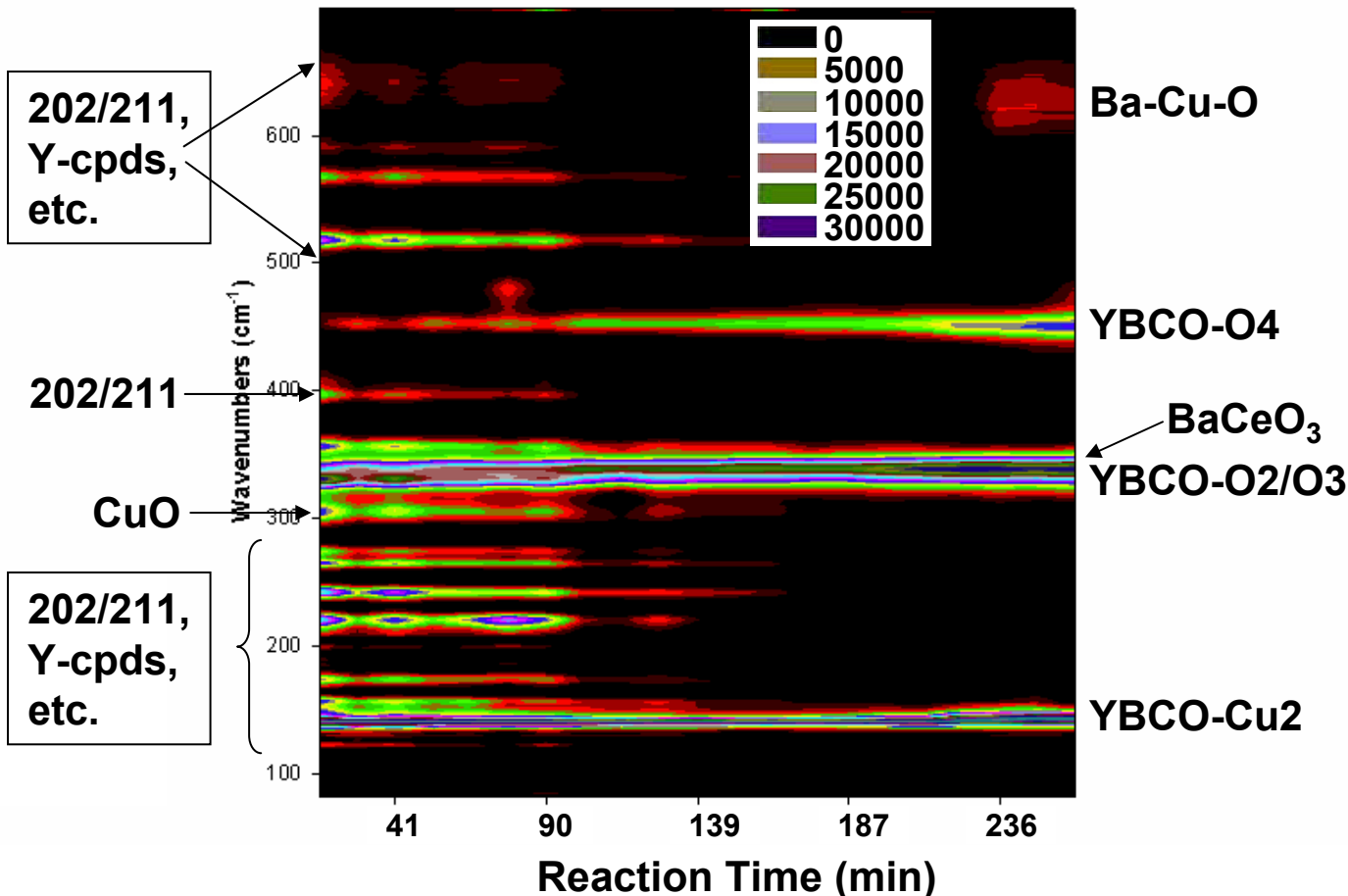
- Predominance of c-axis YBCO growth as well as extent of reaction can be monitored.
- 1  $\mu\text{m}$ -thick YBCO shows disappearance of  $\text{BaF}_2(111)$  and leveling of YBCO(005) at roughly 225 min.
- YBCO (00l) intensity has been found to be closely associated with  $J_c$ .



- However, it is difficult to distinguish and track the presence of other phases that participate in the YBCO formation process.

# Reel-to-Reel Raman is a complementary technique that can provide information not available from XRD

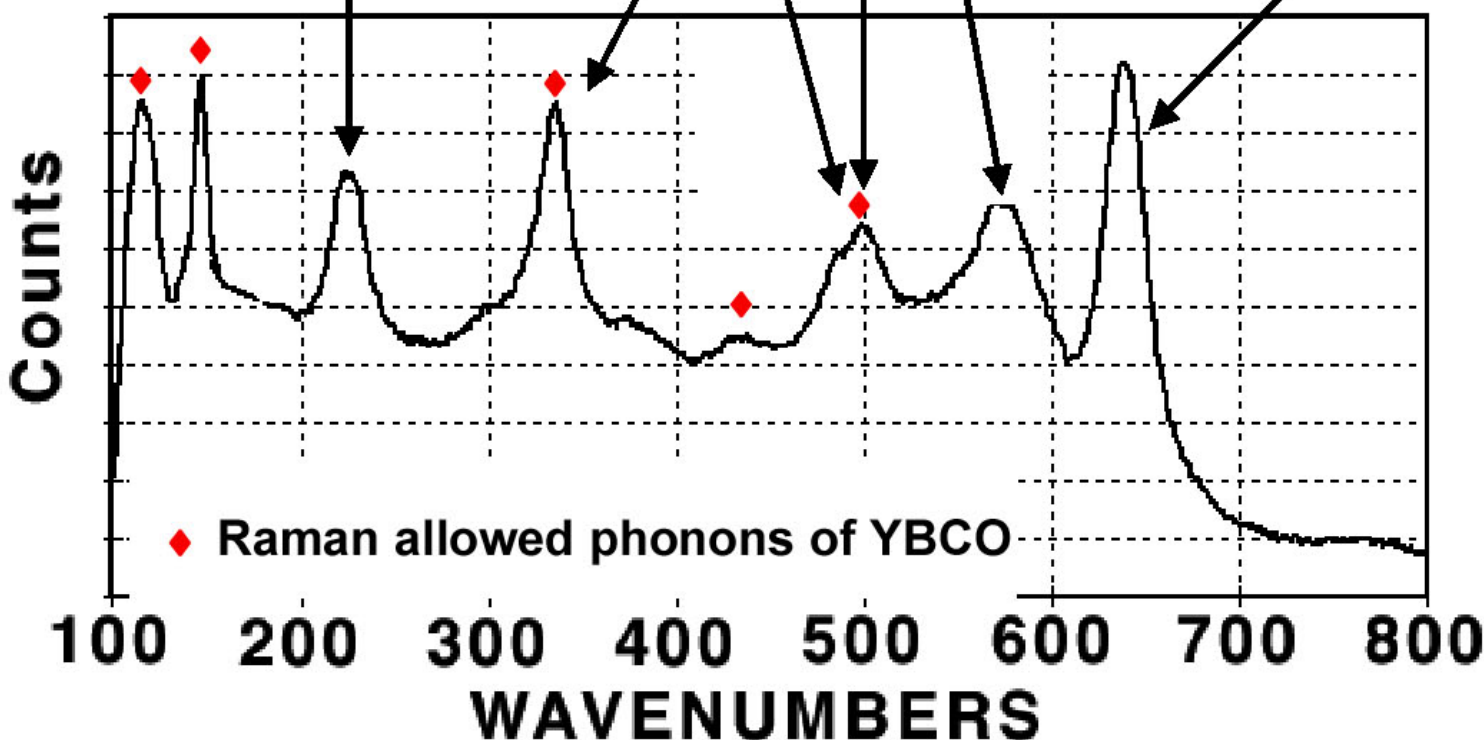
- R-R Raman shows both the phases participating in the reaction (LHS) as well as the products (RHS) as a function of annealing time.
- Raman scans on the same 1  $\mu\text{m}$ -thick tape show that YBCO formation is completed (appearance of Ba-Cu-O) at roughly 230 min.



# Raman Spectroscopy Reveals Many Details about Composition and Microstructure of YBCO Films



- C-axis verticality of YBCO Grains
- Broken M-O Chains / Clumps / Islands /  $\text{BaCuO}_2$
- Oxygen Stiochiometry ( $\text{O}_x$ )
- Cation Disorder (YBCO)
- $\text{BaCuO}_2$



# Grain Boundaries

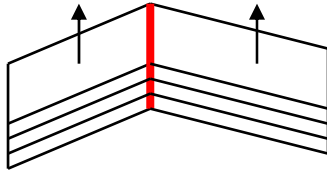
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- Space Charges, Stress, Doping, Oxygenation

ANL, BNL, ORNL, LANL



# Improved interfacial superconductivity via Ca doping

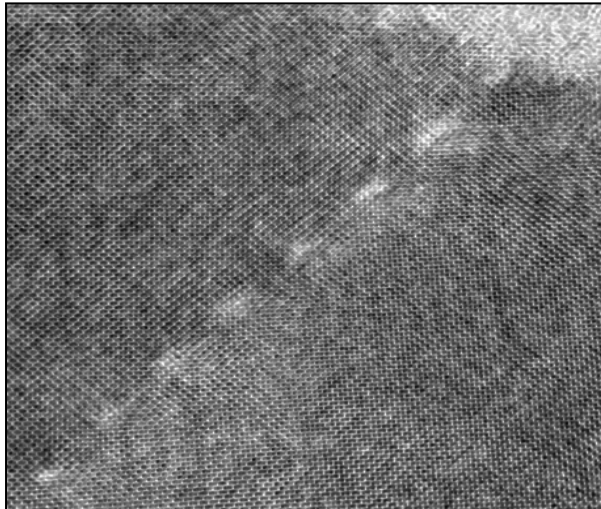


**4° [001] Tilt Boundary**  
**Samples from**  
**C. Joos, Göttingen Univ.**

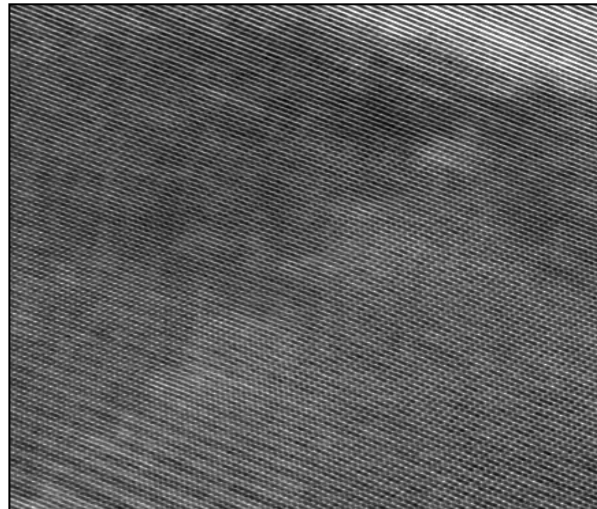
film-GB angle	$J_{gb}^{GB}$ [ $10^6 \text{ Acm}^{-2}$ ]	$J_c$ [ $10^6 \text{ Acm}^{-2}$ ]	$J_{gb}^{GB} / J_c$
undoped 8° [001]	7-11	30-38	0.26
doped 8° [001]	11-21	30-35	0.49
undoped 4° [001]	10-15	25-33	0.43
doped 4° [001]	6-9	10-16	0.58

Critical current densities at 4.2 K for doped and undoped films calculated from *magneto-optical* measurements ( $B_{exp} \approx 100 \text{ mT}$ ).

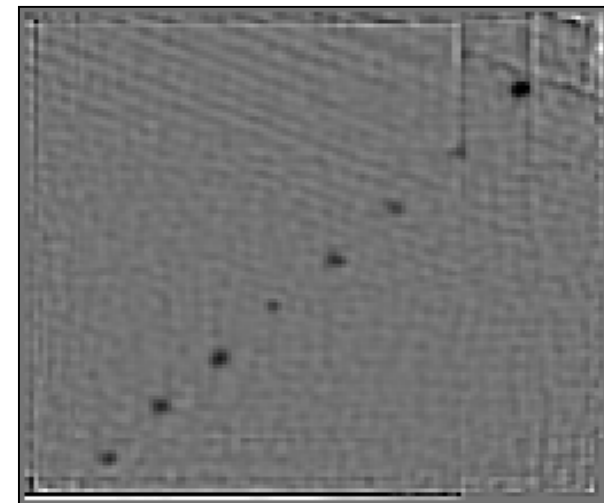
HREM



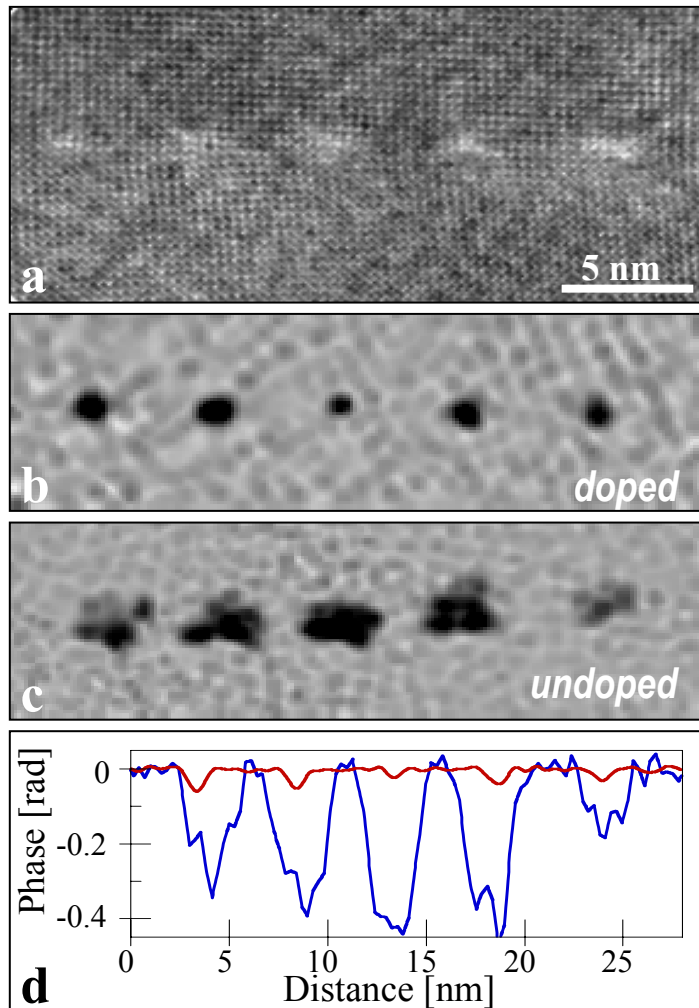
hologram



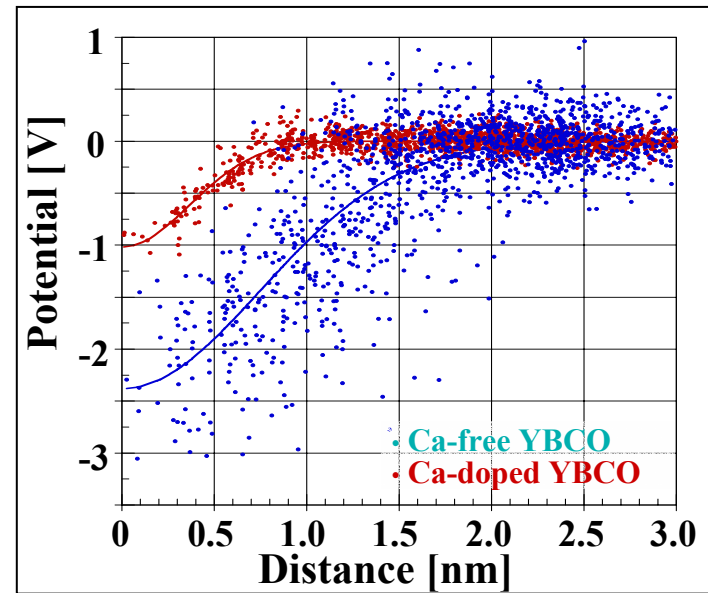
phase



# Electrostatic potential variation : YBCO GB w/o Ca doping



Phase shift from holography



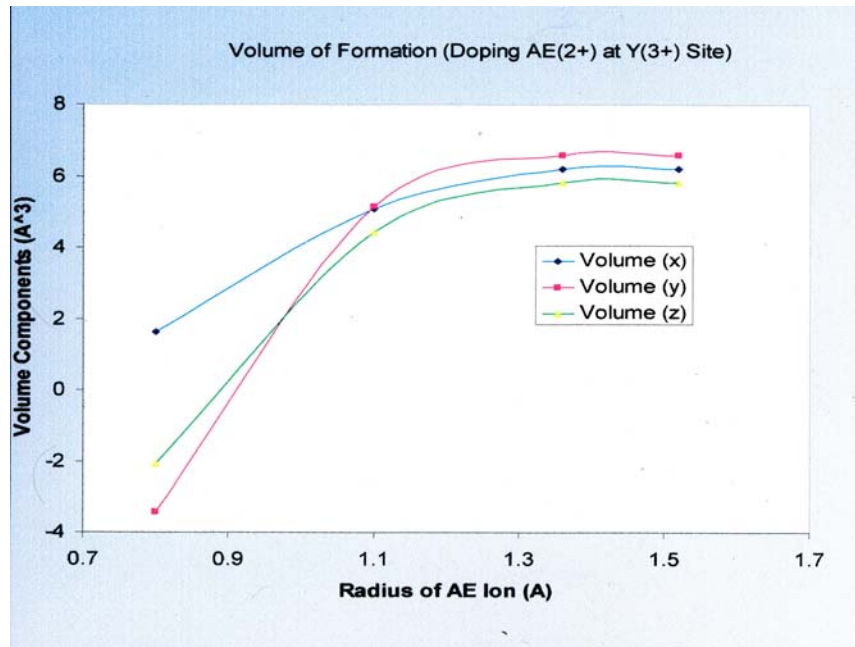
Projected potential around the GB core



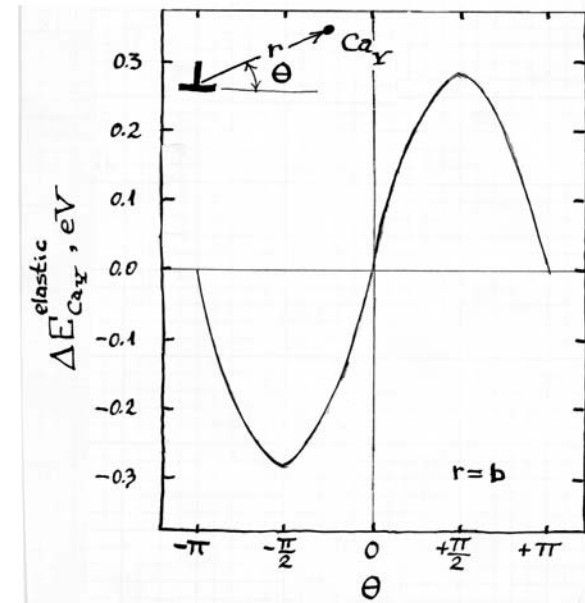
# Theoretical Studies

Stress-Field Interaction with Defects:  $E_{\text{defect}}(\sigma) \cong E_o - \sum_{i,j} \sigma_{ij} V_{ij}$   
 ( $E_o$ ,  $V_{ij}$  computed by atomistic simulation.)

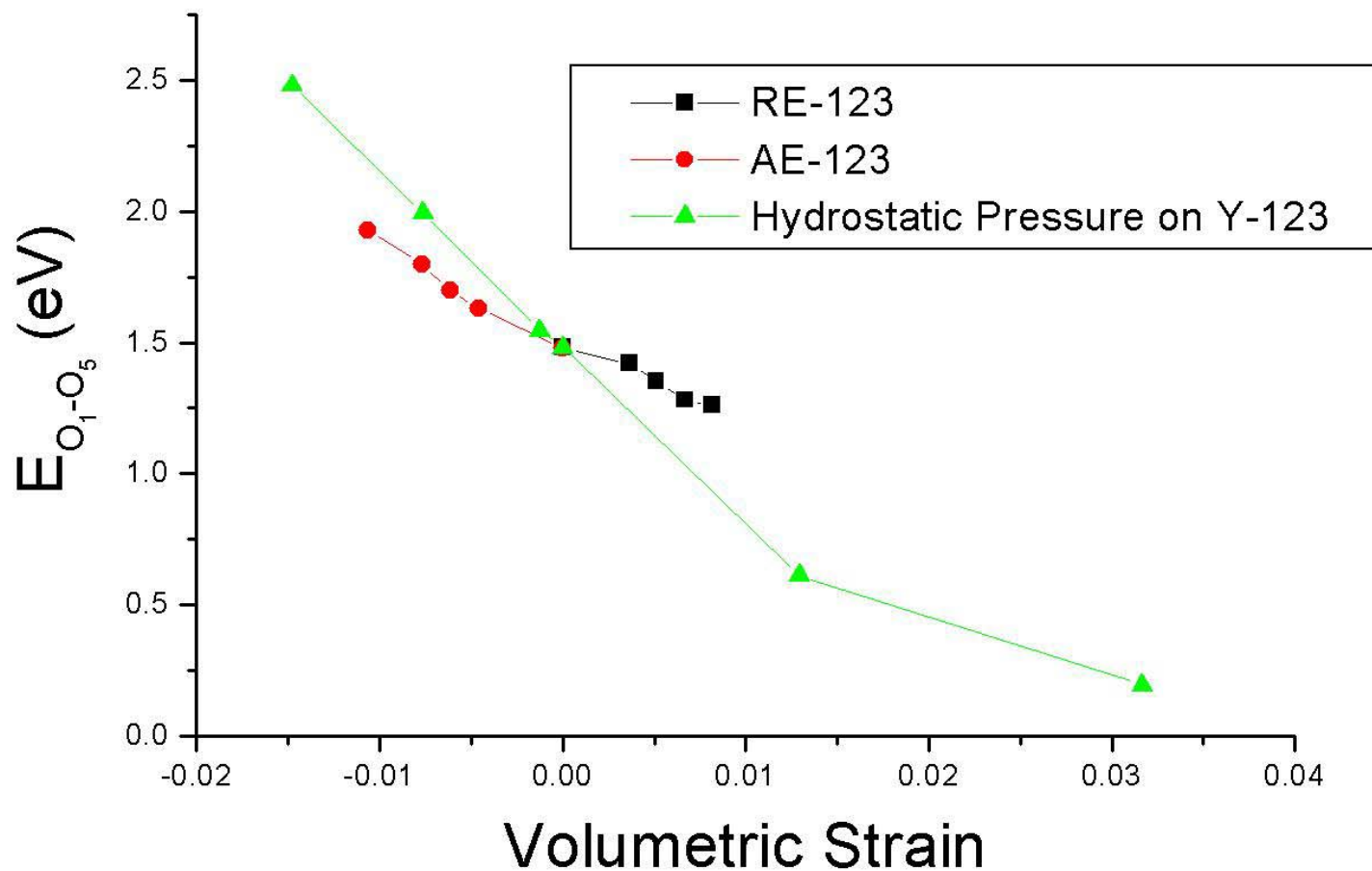
Volume of Formation (Doping AE(2+) at Y(3+) Site)



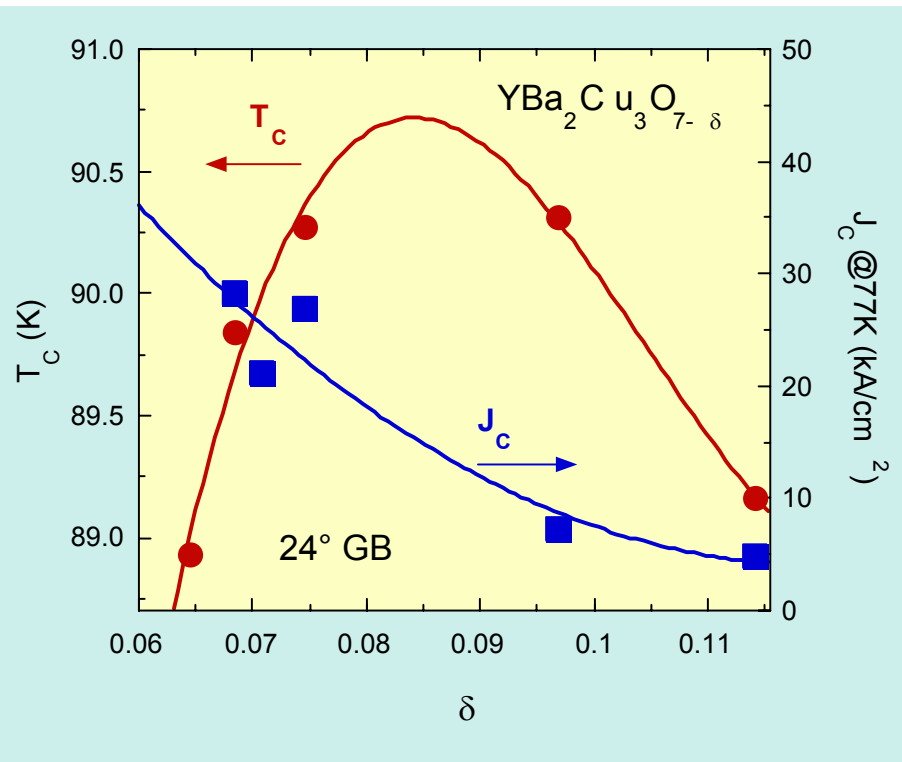
Ca elastic interaction with a dislocation



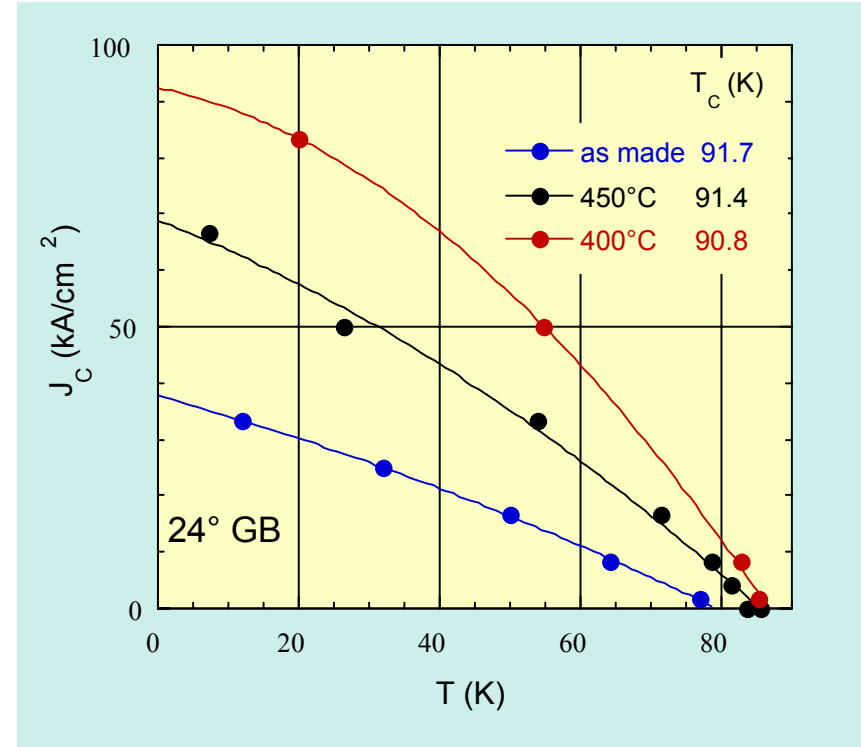
## Frenkel Pair Formation Energy for 123 Phase



## Oxygenation of grain boundaries



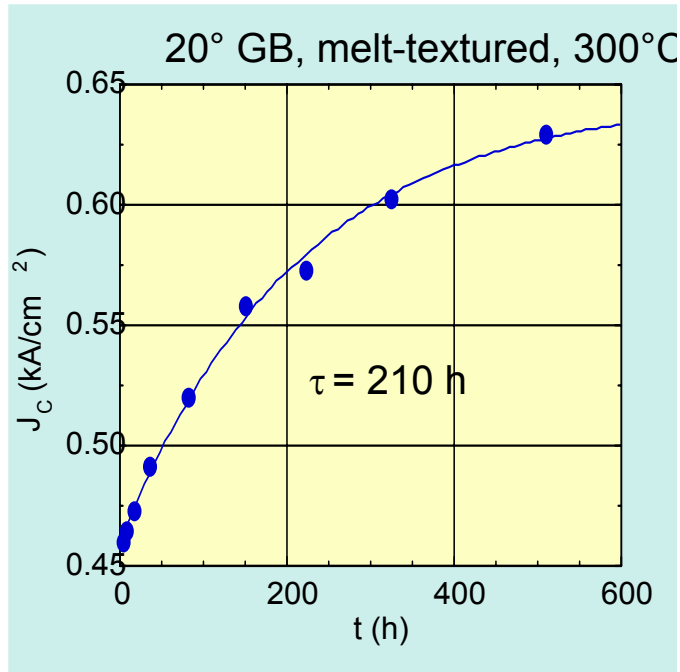
As the oxygen concentration is increased, the film  $T_c$  goes through a maximum at optimum doping. However,  $J_c$  continues to increase in the overdoped regime. Results were obtained from a  $24^\circ$  grain boundary.



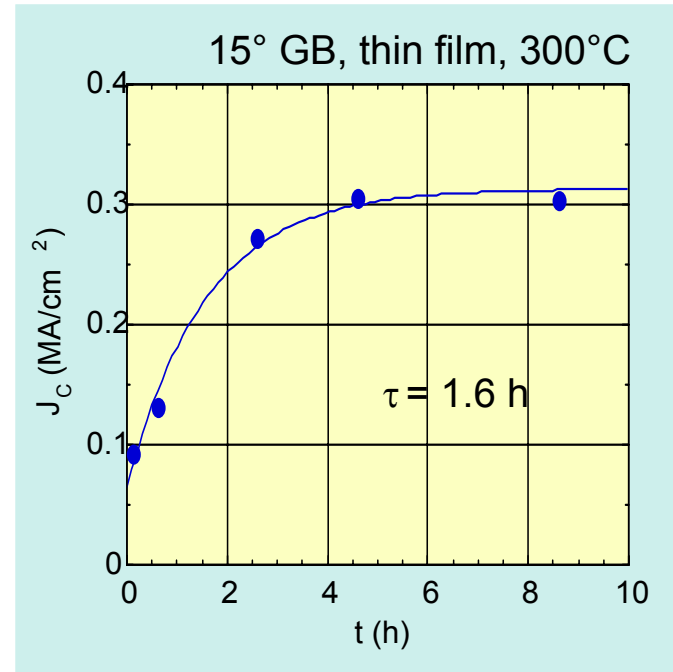
Improvement in  $J_c$  is observed at all temperatures when the level of oxidation is increased. Listed are oxygenation temperatures and  $T_c$  values. Reducing the annealing temperature (e.g., to  $400^\circ\text{C}$  in  $\text{O}_2$ ) increases the oxygen stoichiometry. A smaller enhancement in  $J_c$  is observed as the GB angle becomes smaller.

## Oxygenation of thin film GBs is much faster than bulk GBs

Bulk grain boundary



Thin film grain boundary



Samples were initially equilibrated at 450° in flowing O<sub>2</sub>. They were then oxygenated at 300°C for the indicated times.  $J_c(t) = J_{c0} + \Delta J_c (1 - \exp(-t/\tau))$

- Oxygenation of thin-film GBs is ~ 100 times faster than bulk GBs

# Flux Pinning

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- What pins the flux?  
ANL, BNL, LANL
- Improving flux pinning  
Ames, LANL
- ac losses in thin films  
Ames, BNL, LANL

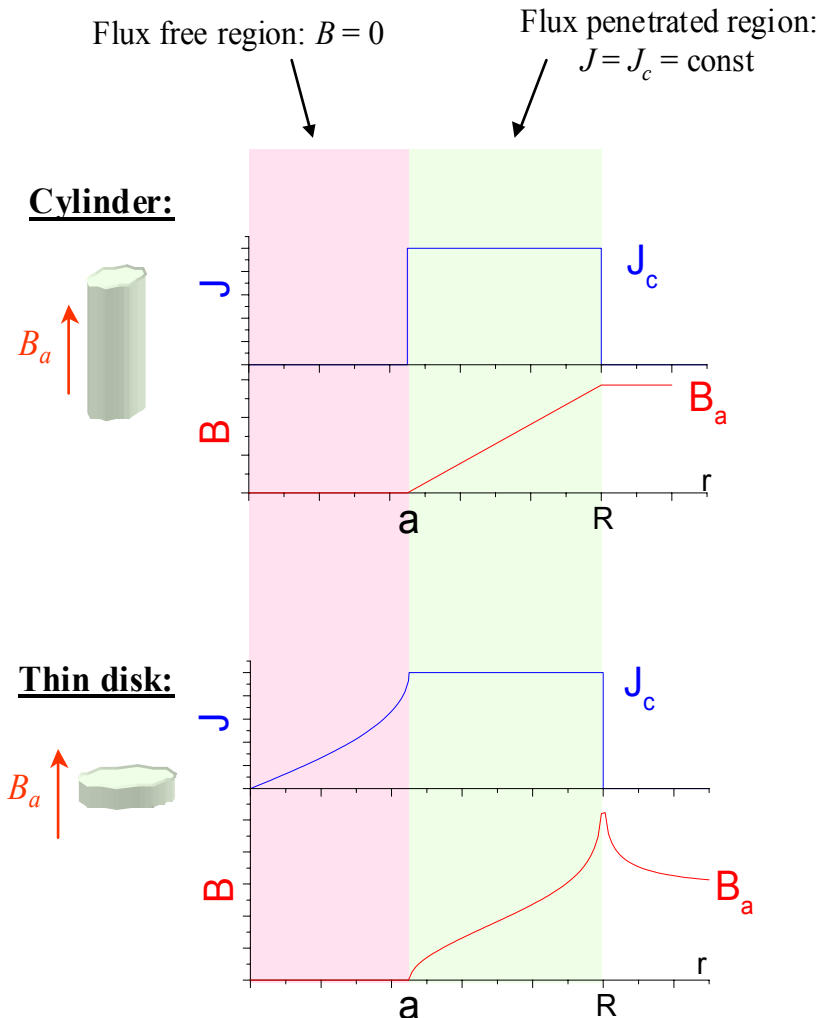
# ac losses in circular disks of YBCO films in perpendicular magnetic fields

M. Suenaga/BNL

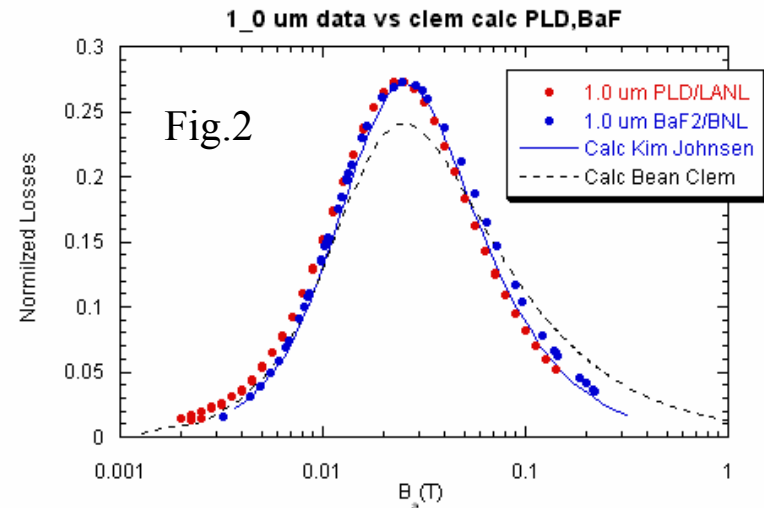
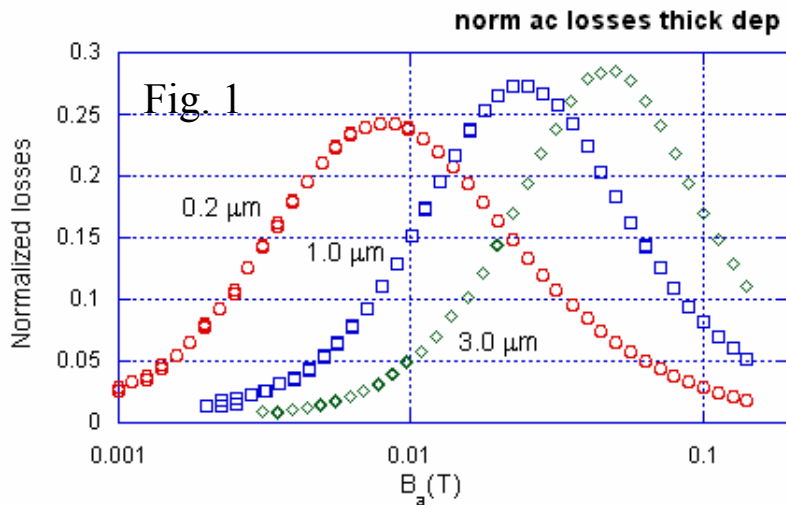
S. R. Foltyn/LANL

The figure illustrates the difference in the magnetic field penetration into a long cylinder and a thin disk. This difference results in significant differences in the properties of superconductors in magnetic fields such as ac losses.

## The Bean model



# ac losses in thin circular disks of YBCO in perp. magn. fields



$$\text{Normalized losses} = [Q(B_a)/(8R/3\pi d)]/(\pi B_a^2/\mu_0)$$

Fig. 1. Thickness dependence of the losses

Fig. 2. Comparisons of theoretical predictions based on the use of the field independent and dependent critical current densities for 1  $\mu\text{m}$  thick films.

YBCO films on  $\text{SrTiO}_3$  by (1) pulsed laser deposition by S. R. Foltyn/LANL and (2)  $\text{BaF}_2$  process by V. F. Solovyov/BNL, and measured by M. Suenaga/BNL

## Conclusions:

- 1) The low field losses are determined by  $1/(J_c d)^2$  rather than  $1/J_c$  for bulk where  $d$  is the thickness of the film.
- 2) The use of the field dependent  $J_c(B)$  is necessary for calculating the losses for moderate to high magnetic fields.

# New Activities in the Final Year Before “Graduation”

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- Quantitative description of nanoscale structure
- A workshop to consolidate what we know and what we don't about the “zoology and ecology” of defects and nanostructure in RE-123 [at BNL, October 2003]
- A review article to summarize where we stand on defects and nanostructures in RE-123